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Thermal conductivity of silicon: theoretical first principles study

***Abstract**. New version of the first principles molecular dynamics calculations of thermal conductivity of materials has been proposed and applied to the silicon crystals. The method proposed is based on the kinetic theory of phonon thermal conductivity and permits to calculate several material properties (specific heat, elastic constant, acoustic velocity, mean phonon relaxation time and coefficient of thermal conductivity) at certain temperature. The method has been applied to the silicon crystal and the results obtained have been found to be in satisfactory agreement with corresponding experimental data. The method proposed is promissing for the ab initio calculations of thermal conductivity of pure and doped semiconductors.*

***Streszczenie**. Zaproponowano nowy sposób obliczeń metodą dynamiki molekularnej z pierwszych zasad współczynnika przewodności cieplnej materiału i zastosowano go do kryształów krzemu. Metoda bazuje na kinetycznej teorii fononowej przewodności cieplnej i daje możliwość obliczenia szeregu własności materiałowych (ciepła właściwego, współczynnika elastyczności, prędkości akustycznej, średniego czasu relaksacji fononów i współczynnika przewodności cieplnej) w określonej temperaturze. Metoda została zastosowana do kryształów krzemu a obliczone wielkości okazały się być zadowalająco bliskie do odpowiednich wartości eksperymentalnych. Zaproponowana metoda może być wykorzystana do obliczeń z pierwszych zasad przewodności cieplnej doskonałych i domieszkowanych półprzewodników. (**Przewodność termiczna krzemu: badania teoretyczne z pierwszych zasad**).*

Keywords: silicon, coefficient of thermal conductivity, molecular dynamics.
Słowa kluczowe: krzem, współczynnik przewodności cieplnej, dynamika molekularna.

Motivation

The silicon (Si) based materials and other wide band gap semiconductors remain the most frequently used substances for the fabrication of different electronic devices. Thermal characteristics of these materials and interfaces between them are therefore of great interest.

Numerous theoretical techniques for determining lattice thermal conductivity have been reported in the literature [1] and have been applied to a wide range of materials. In an equilibrium molecular dynamics (EMD) simulation, the system under investigation has a constant average temperature and an average heat flux of zero [1]. However, at each instant of time a finite heat flux exists due to instantaneous fluctuations in temperature. The popular Green-Kubo method [2, 3], based on the general fluctuation-dissipation theorem [4], relates the lattice thermal conductivity of the system to the time required for such fluctuations to dissipate.

In the present paper, new version of the *ab initio* equilibrium molecular dynamics (AIEMD) method based on the density functional theory (DFT) has been proposed. The method permits to calculate the coefficient of thermal conductivity of a material studied in the framework of the first principles approach. The main advantage of the method proposed is that the only routine EMD run and subsequent calculations of the corresponding values, such as root mean square deviation, mean square displacement, and spectral density of states, are sufficient to obtain the coefficient of thermal conductivity of a material studied. Also, the utilized *ab initio* DFT based approach ensures the universality and relatively high accuracy of the results obtained.

Method and model of calculations

The *ab initio* molecular dynamics (AIMD) simulations of silicon have been performed in the framework of the density function theory (DFT) using the VASP package [5]. The projector augmented-wave (PAW) method with a cutoff energy of 300 eV for silicon for the plane waves was employed [5, 6], together with the corresponding pseudopotentials. For the exchange and correlation terms, the gradient corrected Perdew-Burke-Ernzerhof (PBE) functional was used. Taking the large diamond super cells 3×3×3 of Si into account ($3a$ = 16.45 Å) only the Γ point in the Brillouin zone was considered for geometry optimization. The optimized structures were used as input for the computation of molecular dynamics (MD) trajectories.

The AIMD calculations of Si were performed at the macro-canonical NVE ensemble for different temperatures and initially optimized super cell 3×3×3 at the temperature T = 0 K. Most results of the AIMD calculations have been obtained for the simulation time up to 15 ps with the time step of 1.5 fs. For postprocessing analyses the post MD calculation program used was nMoldyn 3.0 [7].

Using the obtained MD-trajectories the mean-square displacements (MSD) were calculated by the following relation:

$$\sigma^2(t)=\frac{1}{N}\sum_{\alpha=1}^{N} w_\alpha \left\langle d_\alpha^2(t)\right\rangle \tag{1}$$

where, $\left\langle d_\alpha^2(t)\right\rangle$ denotes the MSD for ions of the α-type, $d_\alpha(t)=R_\alpha(t)-R_\alpha(0)$, w_α is the weight coefficient and t the time. The velocity autocorrelation functions (VACF),

$$F_{vv}(t)=\frac{1}{3N}\sum_{\alpha=1}^{N} w_\alpha \left\langle v_\alpha(0)\cdot v_\alpha(t)\right\rangle \tag{2}$$

and the spectral density of states (SDOS) $G(\omega)$, as Fourier transformation of $F_{vv}(t)$,

$$G(\omega)=\int_0^\infty \exp[-i\omega t]F_{vv}(t)dt \tag{3}$$

were calculated. According to Eq. (3) the value of SDOS at ω = 0 gives the diffusion coefficient D_G [7]:

$$D_G=\int_0^\infty F_{vv}(t)dt=G(0) \tag{4}$$

When the above relations are applied to the case of thermal vibrations of atoms in solids without its migration from certain unit cell site, one expects to obtain the phonon characteristics: thermal diffusion coefficient and phonon mean free time.

In the case of relatively slow time dependent decrease of the amplitude of VACF (2) corresponding to a large mean free phonon time τ, the time of MD simulation should be sufficiently large to obtain reliable values of SDOS $G(\omega = 0) = G_0$ using the relation (4). For MSD given, the larger the mean free phonon time τ, the smaller the value $G(\omega = 0)$ is expected. One can use the following time,

$$\tau = \frac{\sigma^2}{6G_0} \tag{5}$$

as the mean free phonon time. The value σ^2 in (5) is the time averaged MSD. The latter relation is similar to the known Einstein-Smoluchowski equation for spatial atomic diffusion, $\sigma^2 = 6Dt$, where D is a diffusion coefficient [8].

According to the kinetic theory of phonon transport [9], the coefficient of thermal conductivity κ is proportional to the mean free phonon path Λ (the average distance between phonon-phonon scattering) or the corresponding mean free phonon time τ,

$$\kappa = \rho C_V v\Lambda/3 = \rho C_V v^2\tau_s/3, \tag{6}$$

where ρ is density of a material, C_V is the specific heat at constant volume V, and v is a mean acoustic phonon velocity. Three temperature dependent values, C_V, v, and τ may be determined separately from the results of *ab initio* MD calculations. The mean free phonon time τ of the relation (5) obtained from MD calculations is expected to be equal to the mean free phonon scattering time τ_s of the relation (6). This is the main idea of the present method.

By performing two sets of MD calculation for two thermostat temperatures T_1 and T_2 at NVT ensemble, one can evaluate the specific heat C_V,

$$C_V = \frac{E_2 - E_1}{m\left(T_2 - T_1\right)} , \tag{7}$$

where E_1 and E_2 are the corresponding total energies and m is mass of crystal supercell.

The acoustic velocity v may be calculated from the elastic constant C and density ρ of a crystal according to the know relation,

$$v = \sqrt{\frac{C}{\rho}} . \tag{8}$$

To estimate the elastic constant C from the results of MD calculations one can use presentations of one atom energy in the forms of (A) thermal energy, $3k_BT/2$, and (B) mechanical energy (kinetic plus potential) of the corresponding effective oscillator, $Kx^2/2 + mv^2/2 = Kx^2$. The characteristic atomic deviation x may be exchanged by the root mean square deviation (RMSD) R obtained from MD calculations at the temperature T (NVT or NPT ensembles),

$$\frac{3k_BT}{2} = KR^2 . \tag{9}$$

Here, the coefficient K is a force constant, the value of which, if obtained, may be used for estimation of the elastic constant C according to the relation,

$$CA = KL , \tag{10}$$

resulted from the definitions of K and C values (A is an aria and L is a length of the model parallelepiped containing one effective oscillator). For silicon diamond structure of the cubic symmetry one can use $A = L^2$. For L value, one can take the nearest neighbor distance $d_{\text{Si-Si}} = L = 2.35$ Å, what is reasonable in view of the oscillator model used.

Thus, on the basis of MD calculations performed at different temperatures one has possibility to estimate, in the framework of the model proposed, the temperature dependent specific heat $C_V(T)$, elastic constant $C(T)$ (11), acoustic velocity $v(T)$ (12), and phonon relaxation time $\tau(T)$ (5) of crystal,

$$C = \frac{3k_BT}{2R^2L} , \tag{11}$$

$$v = \sqrt{\frac{C}{\rho}} = \sqrt{\frac{3k_BT}{2LR^2\rho}} . \tag{12}$$

These values in turn permit one to estimate the temperature dependent coefficient of thermal conductivity $\kappa(T)$ of the crystal studied using the following relation,

$$\kappa = \frac{k_B C_V \sigma^2 T}{12 G_0 R^2 L} . \tag{13}$$

In the present study, the results of AIMD calculations of the thermal conductivity of silicon are obtained in the framework of the above proposed model.

Results and discussion

The distributions $G(f)$ at different temperatures are similar, however clear low frequency shift of the high frequency maximum at $f = 14$ THz is observed. Smaller low frequency shift is observed for the maximum at $f = 4.5$ THz. Simultaneously, no clear temperature widening of $G(f)$ distributions is observed here (Fig. 1). These temperature changes of $G(f)$ may indicate for the decrease of elastic properties of the crystal.

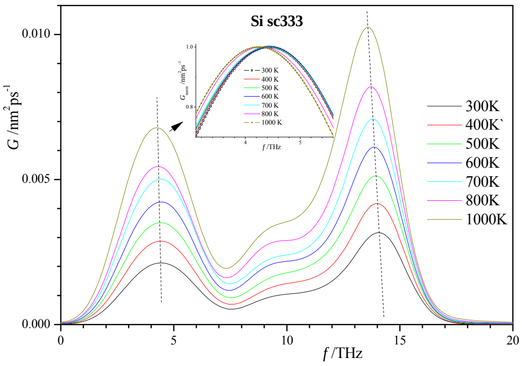

Fig. 1. Density of states $G(f)$ of Si crystal at supercell 3×3×3 for different temperatures. Normalized density of states $G_{\text{norm}}(f)$ in the range of low frequency maximum are presented in the inset

The temperature dependency of specific heat $C_V(T)$ at constant volume V is found to be an increasing function that is generally in agreement with experimental observations (Fig. 2). The absolute calculated values of C_V are however about 30% larger than the corresponding experimental magnitudes C_P (specific heat at constant pressure P) [10, 11]. (For solids, the heat capacities C_V and C_P are close one to another.)

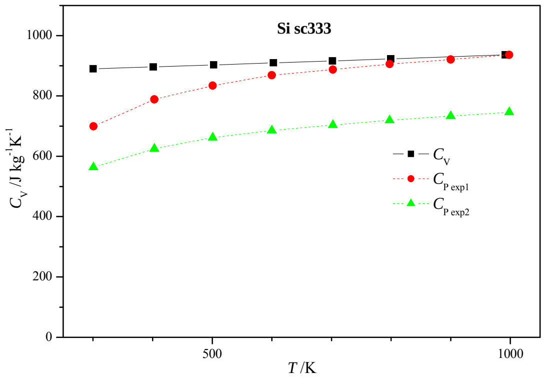

Fig. 2. Temperature dependencies of the calculated (squares) and experimental (circles) [10] and (triangles) [11] specific heat $C(T)$ of Si crystal

The temperature dependency of the calculated elastic constant $C(T)$ of Si has been found to be close to the corresponding experimental data (Fig. 3).

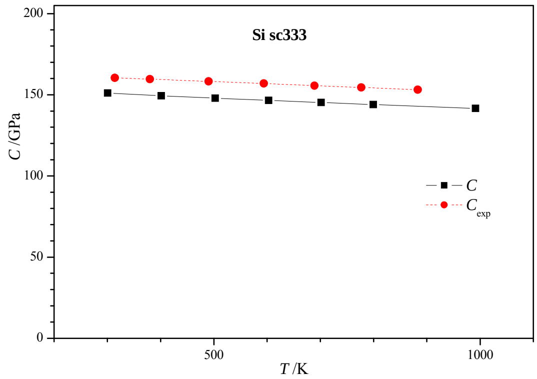

Fig. 3. Temperature dependencies of the calculated (squares) and experimental (circles) [12] elastic constant $C(T)$ of Si crystal

Temperature dependency of the calculated coefficient of thermal conductivity $\kappa_1(T)$ of Si has been found to be a decreasing function, that is similar to the corresponding experimental observation $\kappa_{exp}(T)$ (Fig. 4).

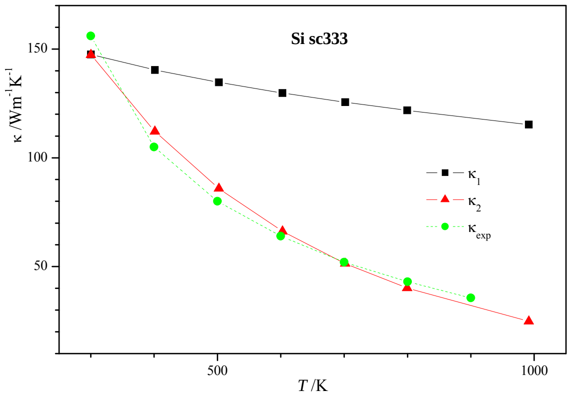

Fig. 4. Temperature dependencies of the calculated (squares) and experimental (circles) [13] coefficient of thermal conductivity $\kappa(T)$ of Si crystal

On the other hand side, the absolute magnitude of temperature decrease for the calculated coefficient $|d\kappa/dT|$ is clear smaller than the similar value for the experimental one (Fig. 4). Taking into account the more close agreements of the calculated temperature dependencies of the heat capacity $C_V(T)$ and elastic constant $C(T)$ (and consequently the acoustic velocity $v(T)$) with corresponding experimental ones discussed above, we have deduced that an estimation of the mean phonon relaxation time τ by the relation (5) is not precise enough, because, at these circumstances, the only temperature dependency $\tau(T)$ may cause large differences between the calculated and experimental temperature dependencies of thermal conductivity, $\kappa_1(T)$ and $\kappa_{exp}(T)$ (Fig. 4). For better matching of the calculated temperature dependency of thermal conductivity to the experimental one $\kappa_{exp}(T)$ [26] the following modification of the relation (5) for the mean phonon relaxation time has been chosen,

$$\tau_2 = \frac{\sigma^2}{6G_0} A\exp\left(-\frac{T}{T_0}\right). \tag{14}$$

The parameters A and T_0 (A = 0.67 , T_0 = 450 K) ensure the best fit of the dependency $\kappa_2(T)$ to the corresponding experimental one $\kappa_{exp}(T)$ [26]. We believe that the relation (14) may be used for the study of thermal conductivity of other silicon based materials and probably materials with similar covalent type chemical bonding.

Conclusions

The routine *ab initio* equilibrium molecular dynamics calculations of silicon crystals permits to calculate several properties (specific heat, elastic constant, and acoustic velocity) related to the calculation of thermal conductivity of the material with the accuracy about 30%.

The relation proposed for calculation of the mean phonon relaxation time of silicon on the basis of the routine *ab initio* molecular dynamics values (mean square displacement and spectral density of states) permits to obtained the absolute values of the mean phonon relaxation time and coefficient of thermal conductivity and the corresponding temperature dependencies in good agreement with experimental data.

The calculations were performed in the computer center ICM of Warsaw University in the framework of the project G26-3.

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